Supporting Information

Electrochemiluminescence immunosensor based on multipath signal catalytic amplification integrated in Cu$^{2+}$-PEI-Pt/AuNCs nanocomposite

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Reagents and apparatus. β2-Microglobulin (β2-MG), Carcinoembryonic antigen (CEA), α1-fetoprotein (AFP) and its antibody were purchased from Biocell Company (Zhengzhou, China). Trisodium citrate (Na$_3$C$_6$H$_5$O$_7$) was got from J&K Scientific Ltd. (Beijing, China). Chloroplatinic acid (H$_2$PtCl$_6$), Chlorauric acid (HAuCl$_4$), bovine serum albumin (BSA) and hydrogen peroxide (H$_2$O$_2$) were bought from Sigma-Aldrich (St. Louis, MO, USA). Phosphate-buffered solution (PBS) parepared by KH$_2$PO$_4$ (0.1 M), Na$_2$HPO$_4$ (0.1 M) and KCl (0.1 M) (pH 7.4, 0.1 M) was used in the this work. The human serum samples were obtained from Southwest Hospital in chongqing.

MPI-E ECL analyzer used for the ECL measurment in this work was obtained from Xi’an Remax Electronic science & Technology Co.Ltd. (potential scanning range: -2~0 V, photomultiplier tube: 800 V). The three-electrode system consist of the modified glassy carbon electrode (GCE, working electrode), Ag/AgCl (sat. KCl, reference electrode) and

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platinum wire (counter electrode) and was used in ECL detection. The scanning electron microscopy (SEM, S-4800, Hitachi, Japan) and X-ray photoelectron spectroscopy (XPS) and were used for characterization of nanomaterials.

**Fig. S1.** CVs curves of bare (a) GCE, (b) GCE/AuNPs, (c) GCE/AuNPs/Ab, (d) GCE/AuNPs/Ab/BSA, (e) GCE/AuNPs/Ab/BSA/AFP in 5 mM [Fe(CN)\textsubscript{6}]\textsuperscript{3-/4-}.

**Fig. S2.** The reproducibility of intra- and inter-assays